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(54) Title: POLYMERIC COMPOSITIONS BASED ON IMPACT RESISTANT VINYL AROMATIC POLYMERS.

(57) Abstract: Polymeric compositions containing: a) 70-97% by weight of a vinyl aromatic polymer modified with rubber; b) 3-30% by weight of a vinyl aromatic polymer with a syndiotactic structure having a melting point higher than 255°C; c) 0-10% by weight with respect to (a) + (b) of a poly phenylene ether; and d) 0-10% by weight with respect to (a) + (b) of an elastomer selected from block copolymers consisting of at least one non-elastomeric polymeric block of a vinyl aromatic monomer and at least one elastomeric block based on a 1,3-conjugated diene.

WO 2004/005397 A1

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POLYMERIC COMPOSITIONS BASED ON IMPACT RESISTANT VINYL AROMATIC POLYMERS.

The present invention relates to a composition based
10 on impact resistant vinyl aromatic polymers.

More specifically, the present invention relates to compositions comprising an impact resistant vinyl aromatic polymer, a vinyl aromatic polymer having a predominantly syndiotactic structure and, possibly, a polyphenyl ether.

15 Compositions based on impact resistant vinyl aromatic polymers and vinyl aromatic polymers having a predominantly syndiotactic structure are known in literature. US patent 6,169,146, for example, describes polymeric compositions having an improved resistance to solvents, containing an
20 atactic polystyrene, possibly impact resistant, in a quantity ranging from 30 to 95% by weight and a syndiotactic polystyrene having a melting point not higher than 255°C, in a quantity ranging from 5 to 70% by weight. The compositions of the known technique can contain, in addition to
25 these two components, one or more of the following addi-

tives selected from a polyphenylene ether, an inorganic filler and a polymer compatible with atactic or syndiotactic polystyrene, having a polar group in the chain.

These compositions, according to the known art, are prepared by kneading the components at a temperature ranging from the melting point of the syndiotactic polystyrene to 270°C.

As the prejudices of the state of the art are reversed, the Applicant has surprisingly found that it is possible to obtain compositions based on atactic or syndiotactic polystyrene with a high resistance to solvents, starting from traditional products, i.e. from a product having a melting point of about 270°C, in the case of syndiotactic polymers. Even more surprisingly, these blends can also be advantageously prepared at temperatures lower than the melting points of the syndiotactic product.

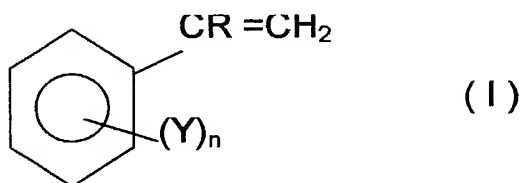
The object of the present invention therefore relates to polymeric compositions comprising:

- a) 70-97% by weight, preferably 75-95%, of a vinyl aromatic polymer modified with rubber;
- b) 3-30% by weight, preferably 5-25%, of a vinyl aromatic polymer having a predominantly syndiotactic structure with a melting point higher than 255°C;
- c) 0-10% by weight with respect to (a) + (b), preferably 0.5-5%, of a polyphenylene ether having an intrinsic

viscosity higher than or equal to 0.1 dl/g measured in chloroform at 25°C;

- d) 0-10% by weight with respect to (a) + (b) of an elastomer selected from block copolymers consisting of at least one polymeric non-elastomeric block of a vinyl aromatic monomer and at least one elastomeric block based on a 1,3-conjugated diene, possibly hydrogenated, having the same or different molecular weight, wherein the diene content is higher than or equal to 50% by weight, preferably between 50 and 90%.

The term "vinyl aromatic polymer", as used in the present description and claims for identifying both components (a) and (b), essentially refers to a product obtained by the polymerization of at least one monomer having the following general formula:



wherein n is zero or an integer ranging from 1 to 5, R is a hydrogen atom or a methyl and Y is a halogen, such as chlorine or bromine, or an alkyl or alkoxy radical having from 1 to 4 carbon atoms.

Examples of vinyl aromatic monomers having the above general formula are: styrene, α -methyl styrene, methyl styrene, ethyl styrene, butyl styrene, dimethyl styrene,

mono-, di-, tri-, tetra- and penta-chloro styrene, bromo styrene, methoxy-styrene, acetoxy-styrene, etc. Styrene and α -methyl styrene are the preferred vinyl aromatic monomers.

The vinyl aromatic monomers having general formula (I) can be used alone or mixed, up to 50% by weight, with other copolymerizable monomers. Examples of these monomers are (meth)acrylic acid, C₁-C₄ alkyl esters of (meth)acrylic acid, such as methacrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, isopropyl acrylate, butyl acrylate, amides and nitriles of (meth)acrylic acid, such as acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, butadiene, ethylene, divinyl benzene, maleic anhydride, etc.. Preferred copolymerizable monomers are acrylonitrile and methyl methacrylate.

The vinyl aromatic polymer, or copolymer, (a) which is obtained has an average molecular weight Mw ranging from 50,000 to 1,000,000, preferably from 70,000 to 300,000.

The vinyl aromatic polymer of step (a) comprises a polymeric matrix wherein a rubber-like phase is dispersed, or grafted, in the form of substantially spherical particles, having an average diameter of between 0.1 and 2 μ m, preferably between 0.2 and 1.2 μ m, in a quantity ranging from 4 and 15% by weight with respect to the total of component (a). The rubber-like phase can be selected from diene rubbers (i) and/or from block copolymers (ii) consist-

ing of at least one non-elastomeric polymeric block of a vinyl aromatic monomer and at least one elastomeric block based on a 1,3-conjugated diene, having the same or different molecular weight, wherein the diene content is equal to
5 or higher than 50% by weight, preferably between 50 and 90%. Further rubbers which can be used as rubber-like phase dispersed in the polymeric matrix are low unsaturated rubbers (iii), such as ethylene/propylene (EPR) or ethylene-propylene-diene (EPDM) rubbers.

10 The diene rubbers are usually of the synthetic type consisting, in particular, of a polymer of a 1,3-conjugated diene containing from 4 to 6 carbon atoms. Examples of these rubbers are polybutadiene and polyisoprene. Polybutadiene is particularly preferred, having:

- 15 - a Mooney viscosity ranging from 20 to 70 ML 1+4 at 100°C, measured according to the ASTM D 1646-80 standard method;
- a viscosity in solution ranging from 40 to 200 cps measured in a solution at 5% by weight in styrene at
20 25°C;
- a 1,2 vinyl content ranging from 5 to 35% wt; and
- a content of 1,4-cis ranging from 20 to 85% by weight.

The block copolymers (ii) are, for example, of the type:

25 S-B; S₁-B-S₂; B₁-S₁-B₂-S₂;

wherein S, S₁ and S₂ represent non-elastomeric polymeric blocks having an average molecular weight Mw ranging from 5,000 to 250,000, whereas B, B₁ e B₂ are elastomeric blocks based on a conjugated diene having an average molecular weight Mw ranging from 2.000 to 250,000.

Particularly preferred block copolymers are those having:

- a Mooney viscosity ranging from 25 to 50 ML 1+4 at 100°C, measured according to the ASTM D 1646-80 standard method;
- a viscosity in solution ranging from 25 to 60 cps, measured in solution at 5% by weight in styrene at 25°C; and wherein
- the polymeric, non-elastomeric block is polystyrene;
- and
- the 1,3-conjugated diene used for the preparation of the elastomeric polymeric block is selected from those having from 4 to 8 carbon atoms. Examples of these dienes are: 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, piperylene and mixtures thereof.

Details on vinyl aromatic polymers modified with a rubber are available in Italian patent 1,264,623 and in European patents 429,986, 716,664 and 286,071.

The vinyl aromatic polymer having a predominantly syndiotactic structure has a melting temperature of about 265-

270°C, an average molecular weight Mw higher than 20,000, generally between 50,000 and 500,000, and a stereo regularity of the syndiotactic type higher than 90%, generally between 95 and 100%. These polymers can be obtained by means of well-known processes described in literature. Syndiotactic vinyl aromatic polymers having the above characteristics can be prepared, for example, by means of a catalytic system based on organometallic complexes of titanium activated by alkyl alumoxanes or fluorinated derivatives of boron, possibly in the presence of alkyl metals as described in US patent 4,680,353 and in the European patent 421,659 or in the US patents 5,629,391, 5,728,784, 5,830,959 and 6,174,973.

The polyphenylene ether used to prepare the polymeric compositions object of the present invention is a well known polymer or co-polymer widely used in industry, especially as engineering polymer, in applications in which impact strength and thermal resistance are required.

Polyphenylene ethers are polymers and co-polymers which comprise several structural units having general formula (II):

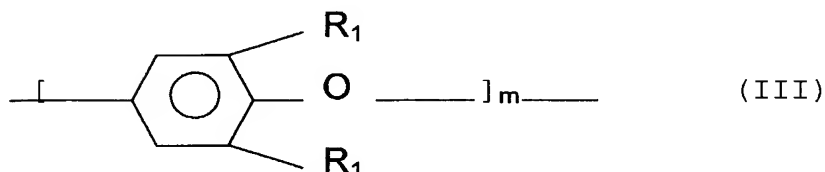


wherein -Ar- represents an arylene radical possibly substituted with one or more halogen atoms, one or more (iso)alkyl or (iso)alkoxyl radicals containing from 1 to 4

carbon atoms, one or more phenyls.

Preferred polyphenylene ethers according to the present invention are those having the following general formula (III):

5



wherein the R_1 radicals independently represent a $\text{C}_1\text{—C}_4$ (iso)alkyl or (iso)alkoxyl radical and m is an integer higher than 50, preferably between 60 and 600.

Illustrative examples of polyphenylene ethers particularly suitable for the present invention are:

- poly(2,6-dimethyl-1,4-phenylene) ether;
- 15 - poly(2,6-diethyl-1,4-phenylene) ether;
- poly(2-methyl-6-ethyl-1,4-phenylene) ether;
- poly(2,6-dipropyl-1,4-phenylene) ether

Poly(2,6-dimethyl-1,4-phenylene) ether is the preferred polyphenylene ether.

20 These polyphenylene ethers generally have an average molecular weight M_w , determined by means of Gel Permeation Chromatography, ranging from 5,000 to 120,000 and their intrinsic viscosity is higher than 0.1 dl/g, preferably between 0.3 and 0.9 dl/g.

25 The polyphenylene ethers used in the composition ob-

ject of the present invention can be prepared by the oxidation of a phenolic compound with oxygen, or a gas containing oxygen, preferably in the presence of a catalyst for oxidative coupling, as described in US patents 3,226,361,
5 3,234,183, 3,306,874, 3,257,357, 3,337,501, 3,956,242, 3,965,069, 4,075,174, 4,102,865, 4,184,034, 4,385,168.

The elastomers (ii), optionally partially hydrogenated, used in combination with the vinyl aromatic polymer modified with rubber, described under item (a), can be used
10 as elastomers (d).

The compositions object of the present invention can also contain, in addition to components (a), (b), (c) and (d), reinforcing additives, such as, for example, glass fibers, carbon fibers, high modulus organic or inorganic fibers, inorganic fillers, flame retardant agents, nucleating
15 agents, dyes, pigments, stabilizers, lubricants, etc. which are well known to technical experts in the field.

The reinforcing additives can generally be used in amounts not higher than 50% by weight, preferably not
20 higher than 30%, with respect to the total composition.

Stabilizers suitable for being used in the compositions of the present invention include a large number of the known thermal stabilizers and oxidation stabilizers used for polyphenylene ether resins or vinyl aromatic polymers. Liquid phosphates, for example, and sterically hin-
25

dered phenols can be added to the compositions of the present invention in a quantity varying from 0.05 to 5% by weight.

The compositions object of the present invention can be prepared with any conventional kneading method. The preparation temperature of the mixture can be maintained, for example, at between 180°C and 300°C or, more preferably, between 180°C and 5°C below the melting point of the vinyl aromatic polymer having a predominantly syndiotactic structure (b). Any kneading unit can be used, operating in continuous or batchwise, such as, for example, twin- or single-screw mixers or extruders. The kneading, moreover, can be carried out in a number of steps as desired, for example by pre-mixing components (a) and (c) and then adding (b); or pre-mixing (b), (c) and (d) and then adding (a), and so on.

The present compositions can be easily processed by injection or extrusion and have a combination of properties which make them suitable for being used for the production of molded articles having a high impact resistance together with a good thermal resistance and resistance to solvents. Thanks to these characteristics, the compositions, object of the present invention, are used in the fields of motor vehicles, household appliances (for example television sets, refrigerators, air conditioners), for the production

of manufactured products which must be oven-painted, parts in contact with engines, household appliances, electronic and technical articles, in the form of cups, boxes, containers, panels, sheets, bars, etc..

5 Some illustrative but non-limiting examples are provided for a better understanding of the present invention and its embodiment. Examples of the materials used and details on the characterization of the samples are provided below.

10 Materials:

Impact resistant atactic polystyrene: commercial product Edistir RR 745 (Polimeri Europa);

Atactic polystyrene: commercial product Edistir N 1782 (Polimeri Europa);

15 Syndiotactic polystyrene: polymer obtained from the polymerization of styrene in the presence of $\text{Cp}^*\text{TiCl}_3/\text{MAO}$ ($T_m=273^\circ\text{C}$, $M_n=230,000$);

SEBS (block styrene-hydrogenated butadiene elastomer): commercial product Kraton G 1652 (Kraton Polymers);

20 Poly(2,6-dimethyl-1,4-phenylene ether): commercial product PPO H 51 (Mitsubishi).

Characterization

The mechanical properties were determined according to ISO 180 (Izod Impact Strength) and ISO 527 (Tensile Test)
25 on ISO 3167 injection molded test samples.

The resistance to solvents (ESCR, Environmental Stress-Cracking Resistance) was determined on the same test samples according to two different procedures.

1) Blistering tests

5 The procedure used contemplates the deposition, by means of a pipette, of 1 to 6 drops of cyclopentane in several numbered positions (from 1 to 6), at a frequency of 1 drop per minute. The samples are placed in an oven at 60°C for 15 minutes in order to release the cyclopentane penetrated.

10 After extraction from the oven, the materials are compared, and the sample which starts forming blisters at the highest number of drops, is considered as being the best, using a parameter obtained by the sum of the number corresponding to the position in which corrosion of the test

15 sample surface is observed and of that corresponding to complete blisters: the value of 7 corresponds to "no effect observed". Consequently, the values which represent solvent resistance range from 2 (very poor resistance) to 14 (perfect resistance).

20 Repeated tests confirmed the good reproducibility of the method.

2) ESCR tests

5 test samples of each specimen are clamped in a vice which bends them under flexion so that the external surface

25 reaches a deformation level equal to 0.7%. A drop of cyclo-

pentane is dripped every 5 minutes onto this surface in a central position with respect to the length of the test sample. After 15 minutes (and consequently after 3 drops of cyclopentane), the test samples are extracted from the vice
5 and subjected to tensile stress according to ISO 527. As a result of the test, the following values are obtained:

- a) elongation to break, after exposure to solvent under deformation:
- b) the ratio between this value and that of the elonga-
10 tion to break according to ISO 527 on test samples not exposed (residual elongation).

Example 1

A blend based on 4,500 g of Edistir RR745 impact resistant polystyrene and 500 g of syndiotactic polystyrene
15 was prepared in a Berstorff ZE 25 twin-screw extruder. The temperature profile in the nine zones of the extruder was the following: 200-220-240-250-260-260-260-260-250°C.

Comparative example

Example 1 was repeated, but using Edistir 1782 atactic
20 polystyrene instead of 500 g of syndiotactic polystyrene.

Example 2

Example 1 was repeated, but using the following temperature profile of the extruder:

210-245-265-275-285-285-285-285-275°C.

25 Example 3

Example 2 was repeated, but using 3,600 g of Edistir RR745 impact resistant polystyrene and 900 g of syndiotactic polystyrene.

Example 4

5 Example 1 was repeated, but using 4,350 g of Edistir RR745 impact resistant polystyrene, 250 g of Kraton G1652 (block styrene-hydrogenated butadiene elastomer), 400 g of syndiotactic polystyrene.

Example 5

10 Example 1 was repeated, but using 4,350 g of Edistir RR745 impact resistant polystyrene, 200 g of PPO H 51, 400 g of syndiotactic polystyrene and 50 g of aluminum tert-butyl benzoate.

Example 6

15 Example 2 was repeated, but using 4,350 g of Edistir RR745 impact resistant polystyrene, 250 g of Kraton G1652, 400 g of syndiotactic polystyrene.

The results of the tests described in the above examples are indicated in the following table.

20

25

Table

	Ex. 1	Comp.	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
IZOD (kJ/m ²)	6.3	5.5	5.7	5.4	8.0	6.7	7.3
Tensile modulus (MPa)	1550	1490	1550	1680	1480	1580	1510
ESCR (Blistering test)	14	5	14	14	14	14	14
Yield stress (MPa)	19.2	18.9	20.3	22.5	18.3	19.5	20.5
Elongation to break (%)	29	46	37	34	45	32	44
Elongation to break after exposure to cyclopentane (%)	30	29	35	31	43	32	43
Residual elongation (%)	106	64	94	91	96	100	98

CLAIMS

1. Polymeric compositions containing:

a) 70-97% by weight, preferably 75-95%, of a vinyl aromatic polymer modified with rubber;

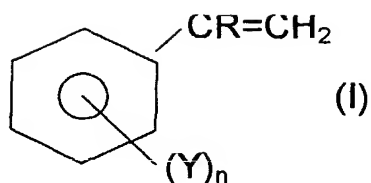
5 b) 3-30% by weight, preferably 5-25%, of a vinyl aromatic polymer having a predominantly syndiotactic structure and a melting point higher than 255°C;

c) 0-10% by weight with respect to (a) + (b), preferably 0.5-5%, of a polyphenylene ether having an intrinsic
10 viscosity higher than or equal to 0.1 dl/g, in chloroform at 25°C; and

d) 0-10% by weight with respect to (a) + (b) of an elastomer selected from block copolymers consisting of at least one non-elastomeric polymeric block of a vinyl
15 aromatic monomer and of at least an elastomeric block based on a 1,3-conjugated diene, possibly hydrogenated, having the same or different molecular weight, whose diene content is higher than or equal to 50% by weight, preferably between 50 and 90%.

20 2. The compositions according to claim 1, wherein the vinyl aromatic polymer is a product obtained from the polymerization of at least one monomer having the following general formula:

25



5 wherein n is zero or an integer ranging from 1 and 5, R is a hydrogen atom or a methyl and Y is an halogen, such as chlorine or bromine, or an alkyl or alkoxy radical having from 1 to 4 carbon atoms.

3. The compositions according to claim 1 or 2, wherein
10 the vinyl aromatic polymer, or copolymer, (a) has an average molecular weight Mw ranging from 50,000 to 1,000,000.

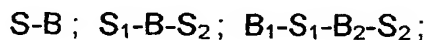
4. The compositions according to any of the previous claims, wherein the vinyl aromatic polymer of step (a) comprises a polymeric matrix in which a rubber-like phase is
15 dispersed, or grafted, under the form of substantially spherical particles having an average diameter of between 0.1 and 2 μm , in an amount ranging from 4 to 15% by weight with respect to the total of component (a).

5. The compositions according to claim 4, wherein the
20 rubber-like phase is selected from diene rubbers (i) and/or block copolymers (ii) consisting of at least one non-elastomeric polymeric block of a vinyl aromatic monomer and at least one elastomeric block based on a 1,3-conjugated diene, having the same or different molecular weight, whose
25 diene content is higher than or equal to 50%.

6. The compositions according to claim 4, wherein the rubber-like phase dispersed in the polymeric matrix consists of low unsaturated rubbers (iii) such as ethylene/propylene rubbers (EPR) or ethylene/propylene/diene rubbers (EPDM).

7. The compositions according to any of the claims from 1 to 5, wherein the diene rubbers are generally of the synthetic type consisting of a polymer of a 1,3-conjugated diene containing from 4 to 6 carbon atoms.

8. The compositions according to any of the claims from 1 to 5, wherein the block copolymers (ii) are of the type :



wherein S, S₁ and S₂ represent non-elastomeric polymeric blocks having an average molecular weight Mw ranging from 5,000 to 250,000, whereas B, B₁ e B₂ are elastomeric polymeric blocks based on a conjugated diene having an average molecular weight Mw ranging from 2,000 and 250,000.

9. The compositions according to any of the previous claims, wherein the vinyl aromatic polymer having a predominantly syndiotactic structure has a melting temperature of about 265-270°C, an average molecular weight Mw higher than 20,000 and a syndiotactic stereo regularity higher than 90%.

10. The compositions according to any of the previous claims, wherein the polyphenylene ether includes several

structural units having general formula (II)



wherein -Ar- represents an arylene radical possibly substituted with one or more halogen atoms, one or more
5 (iso)alkyl or (iso)alkoxyl radicals containing from 1 to 4 carbon atoms, one or more phenyls.

11. The compositions according to claim 10, wherein the polyphenylene ethers have an average molecular weight Mw, determined by means of Gel Permeation Chromatography, rang-
10 ing from 5,000 to 120,000 and their intrinsic viscosity is between 0.3 and 0.9 dl/g.

12. The compositions according to any of the previous claims, wherein the elastomer (d) is selected from the elastomers (ii), optionally partially hydrogenated, used in
15 combination with the vinyl aromatic polymer modified with rubber of step (a).

13. A process for the preparation of the compositions according to any of the previous claims, which includes kneading the components at a temperature ranging from 180°C
20 to 300°C.

14. The process according to claim 13, wherein the kneading temperature ranges from 180°C to 5°C below the melting point of the vinyl aromatic polymer having a predominantly syndiotactic structure (b).

25 15. Use of the compositions according to any of the previ-

ous claims in the manufacturing of molded articles having impact and thermal resistance, and resistance to solvents.

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 03/06840

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L25/06 //(C08L25/06,25:06)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; OKADA, AKIHIKO ET AL: retrieved from STN Database accession no. 138:25359 HCA XP002258086 abstract -& WO 02 098960 A (IDEMITSU PETROCHEMICAL CO., LTD., JAPAN) 12 December 2002 (2002-12-12) claims; examples; tables --- -/--</p>	1-15

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

16 October 2003

Date of mailing of the international search report

03/11/2003

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 03/06840

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; OKADA, AKIHIKO ET AL: retrieved from STN Database accession no. 137:279959 HCA XP002258087 abstract -& WO 02 077098 A (IDEMITSU PETROCHEMICAL CO., LTD., JAPAN) 3 October 2002 (2002-10-03) claims; examples; tables ---</p>	1-15
X	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; YAMAZAKI, MICHIAKI ET AL: retrieved from STN Database accession no. 136:310884 HCA XP002258088 abstract -& JP 2002 113756 A (IDEMITSU PETROCHEMICAL CO., LTD., JAPAN) 16 April 2002 (2002-04-16) paragraph '0047!; claims ---</p>	1-15
X	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; AOYAMA, TAKUMA ET AL: retrieved from STN Database accession no. 134:281621 HCA XP002258089 abstract -& WO 01 25329 A (IDEMITSU PETROCHEMICAL CO., LTD., JAPAN) 12 April 2001 (2001-04-12) claims; examples; tables ---</p>	1-15
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EUR-CL (EPC) : C08L025/06 , C08L025/06

ABSTRACT:

CHG DATE=20040203 STATUS=O>Polymeric compositions containing: a) 70-97% by weight of a vinyl aromatic polymer modified with rubber; b) 3-30% by weight of a vinyl aromatic polymer with a syndiotactic structure having a melting point higher 15 than 255°C; c) 0-10% by weight with respect to (a) + (b) of a poly- phenylene ether; and d) 0-10% by weight with respect to (a) + (b) of an elas- tourer selected from block copolymers consisting of at least one non-elastomeric polymeric block of a vinyl aromatic monomer and at least one elastomeric block based on a 1,3-conjugated diene.